Self Powered Humidity Sensors Based on Zero Dimensional Perovskite-like Structures With Fast Response and High Stability

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Methods and materials:

Methylamine (33 wt% in ethanol), Hydriodic acid (HI, 57 wt% in water), Lead Iodide (PbI_2, 99%) and N-N-Dimethylformamide (DMF, anhydrous 99.8%) were purchased from Sigma Aldrich. Fluorine doped tin oxide (FTO) glass substrates were purchased from Greatcell Solar (Australia).

CH_3NH_3I (MAI) synthesis

38 mL Methylamine was taken in a 100 mL round bottomed flask. It was cooled to 5 ^oC in an ice bath. Under vigorous stirring (500 rpm), 40 mL Hydriodic acid was added dropwise. After complete addition of HI, the reaction mixture was left for stirring for another two hours. Following this, the solvent was evaporated at 60 ^oC using a rotary evaporator and the formed MAI was purified using Diethyl ether. It was recrystallized and dried for 24 h at 60 °C in a vacuum oven prior to use.

Preparation of MA_4PbI_6:

MAI and PbI_2 were mixed in a ratio 4:1 in DMF to prepare the MA_4PbI_6 solution.

Device fabrication

Using an IR Laser, FTO substrates were etched. The dimension of the substrate was 2 cm X 2 cm with an etch width of 80 μm in the center. These substrates were cleaned using an ultra-sonicator with the following solutions- soap, DI water, acetone and ethanol for 10 minutes each. The substrate was further sintered at 500 ^oC for 30 minutes. MA_4PbI_6 solution was deposited via spin coating at a speed of 3000 rpm and an acceleration of 1000 rpm/s for 30s. This film was annealed for 15 minutes at 70 ^oC. This fabricated device was used for all the electrical characterizations. For the measurements of humidity response to human skin and breath, the device is also coated with porous PMMA layer on top of the sensing material. Porous PMMA layer is deposited by keeping the spin coated film immediately under vacuum.

Humidity Modifications for the Experiments

For the images of the film, UV-Vis absorption, PL spectroscopy, Voltage and current versus time measurements, dynamic voltage and current reversibility studies, response and recovery studies and XRD characterizations, the different humidity levels were established by carrying water vapour over N_2 carrier gas. The humidity levels were calibrated using a standard humidity sensor. For the IV, the humidity levels were achieved using saturated salt solutions. The salt solutions along with the humidity levels supplied by them are provided in the table below.

Saturated Salt solution (at 25 °C ± 3 °C)	Humidity level (% RH)
LiCl	11
$MgCl_2$	33
K_2CO_3	43
NaBr	57
$CuCl_2$	65
NaCl	75
KCl	85

Characterization

The X-ray diffraction (XRD) studies were carried out using Rigaku Smartlab instrument with a Cu Kα source of wavelength, λ=0.154 nm. The electrical characterizations were carried out

using a Keithley 2450 Multimeter (Keithley, USA). The UV-Vis Absorption studies were carried out using a Shimadzu UV-2600 spectrophotometer. The Photoluminescence measurements were carried out using a Horiba Fluoromax spectrophotometer. The SEM images were taken using Zeiss Ultra 55 Scanning Electron microscope.

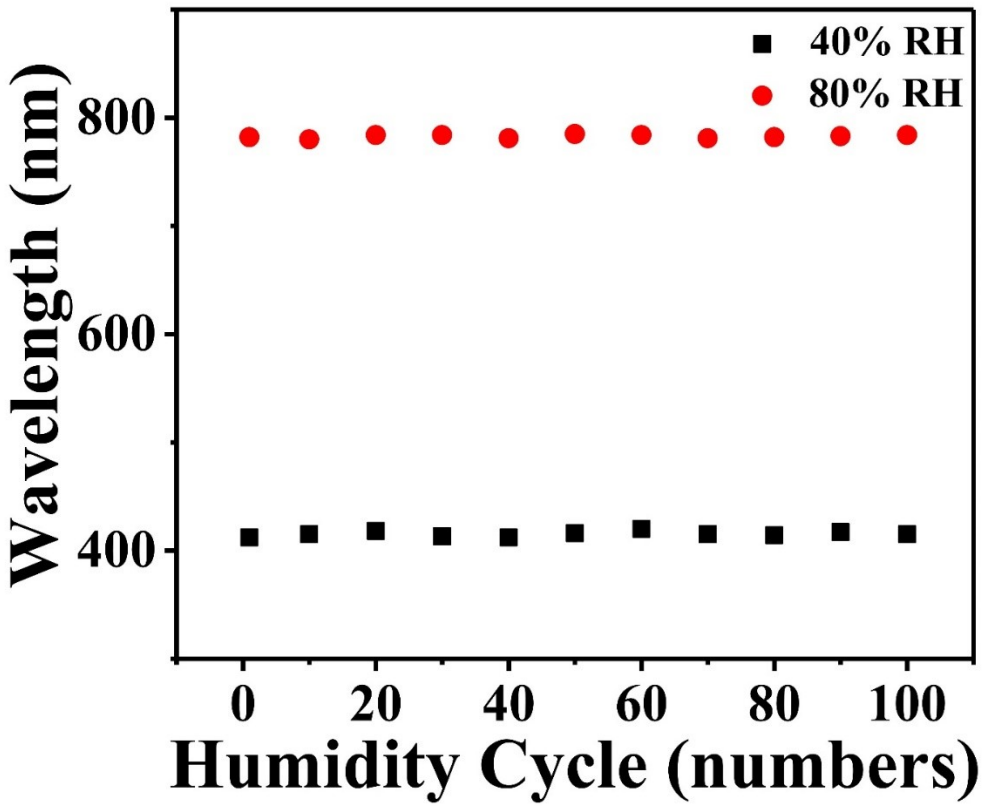

Figure S1: Absorption onset values for 100 cycles at 40% RH and 80% RH.

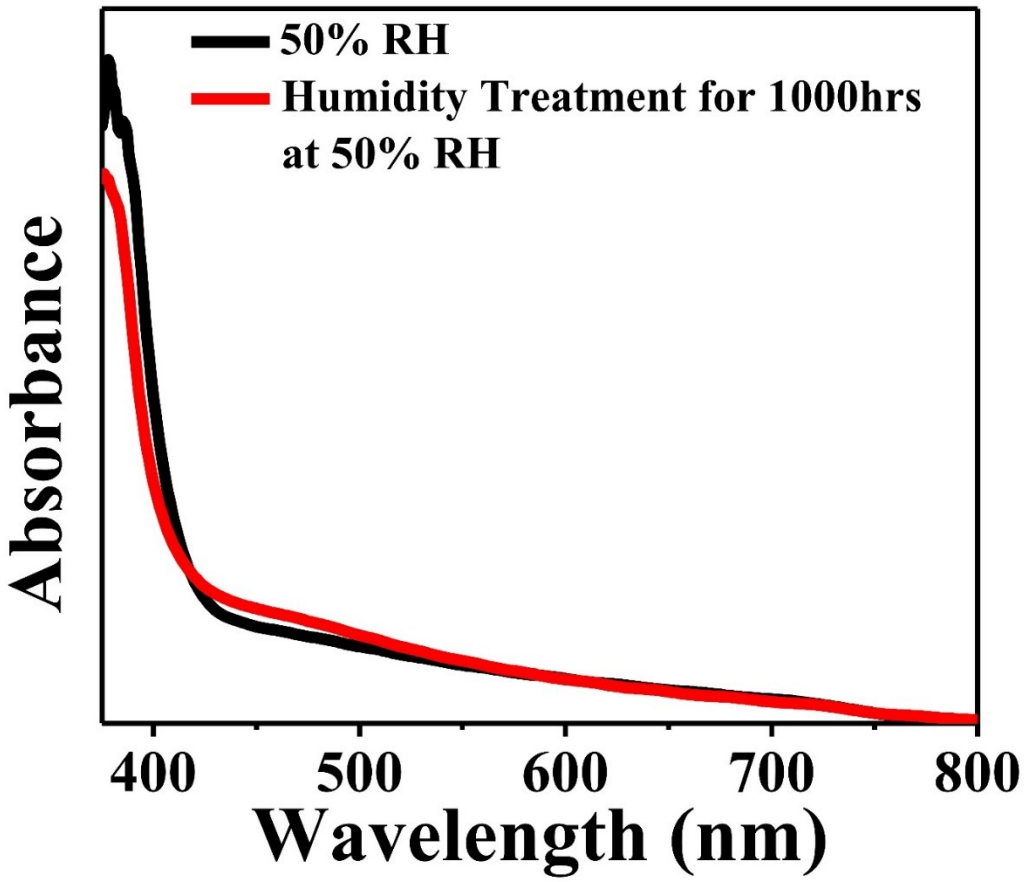

Figure S2: Absorption spectra of as prepared $(MA)_4PbI_6.2H_2O$ film at 50% RH and after humidity treatment for 1000 hours at 50% RH.

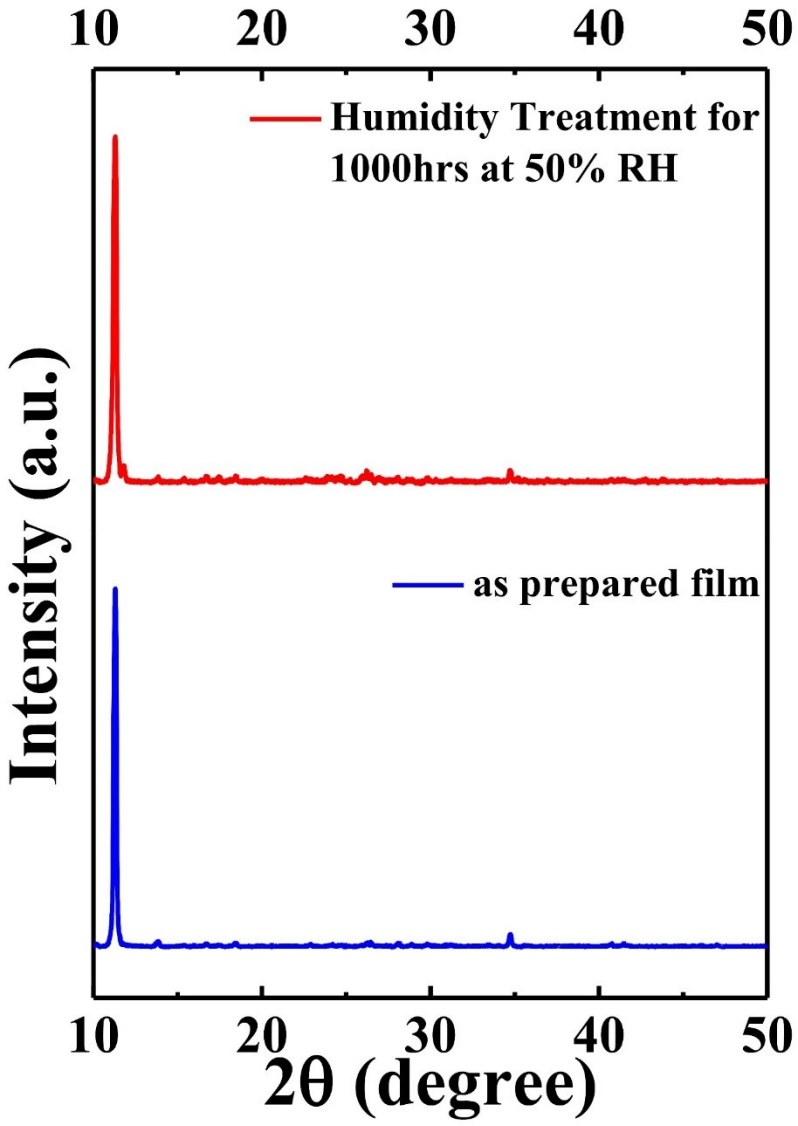

Figure S3: XRD spectra of as prepared $(MA)_4PbI_6.2H_2O$ film at 50% RH and after humidity treatment for 1000 hours at 50% RH.

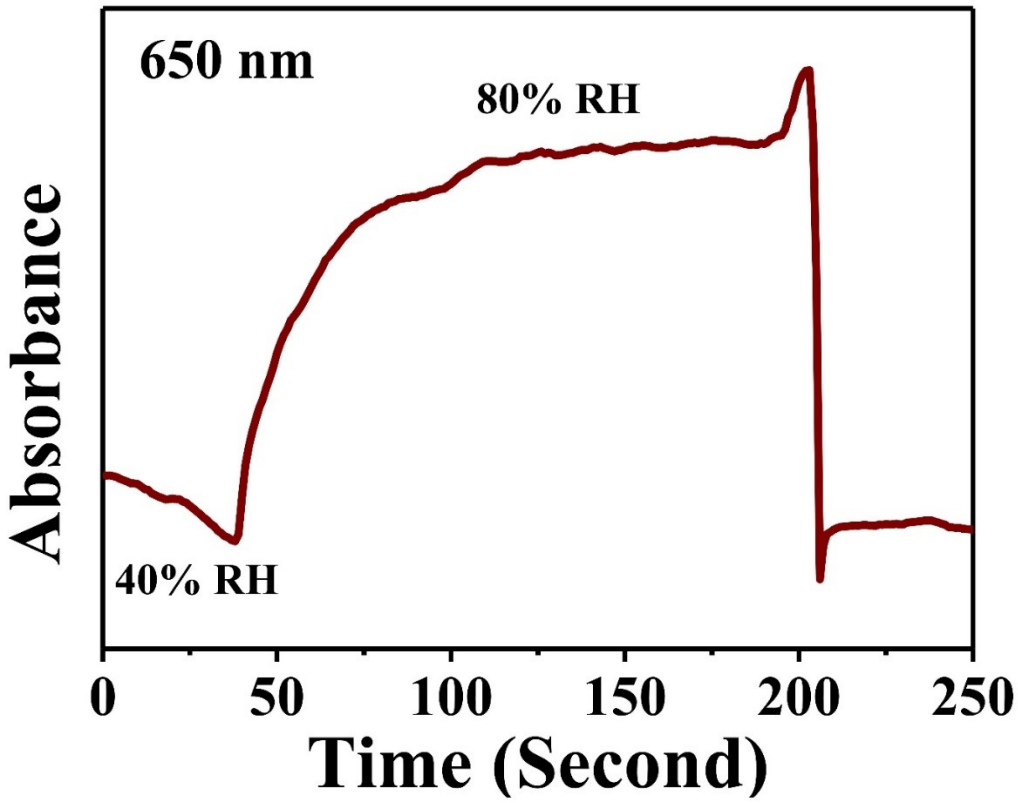

Figure S4: Absorption of $(MA)_4PbI_6.2H_2O$ film at 650 nm wavelength between 80% RH and 40% RH.

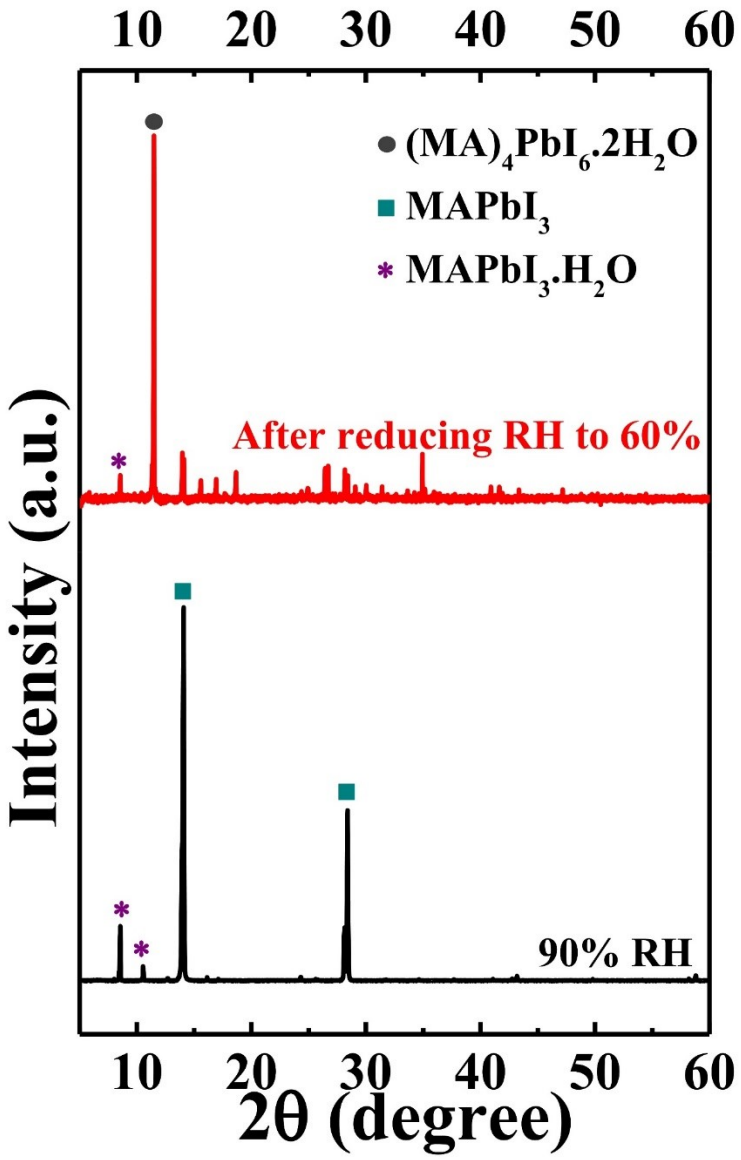

Figure S5: XRD spectra of $(MA)_4PbI_6.2H_2O$ film at 90% RH and after reducing humidity to 60% RH.

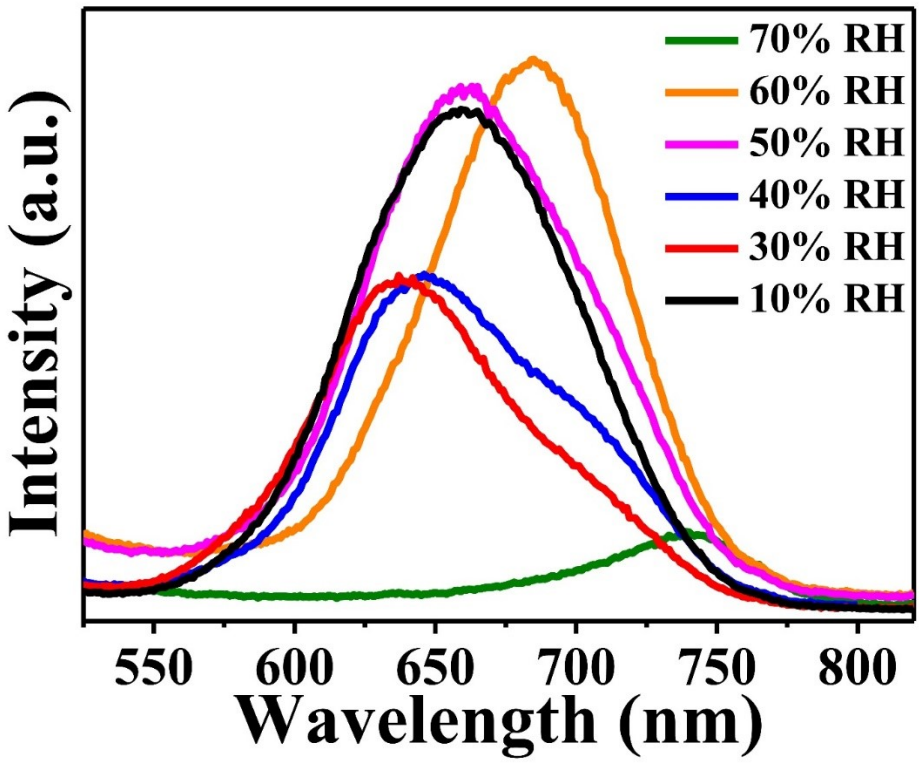

Figure S6: Photoluminescence spectra of $(MA)_4PbI_6.2H_2O$ film at different RH measured from high humidity to low humidity.

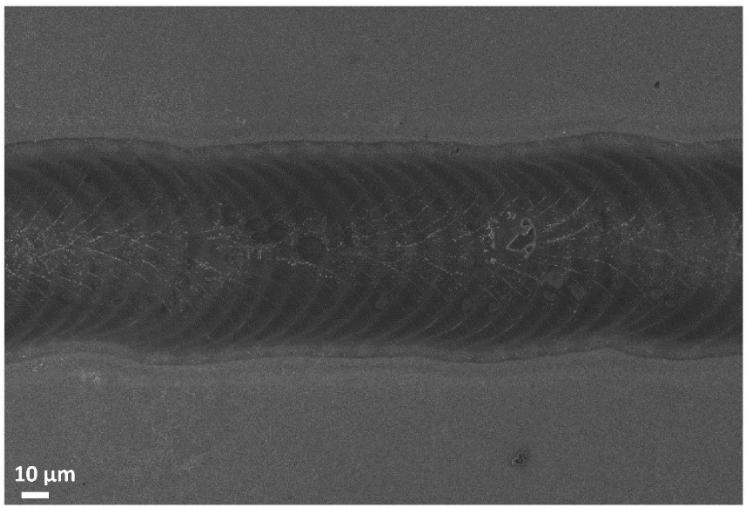

Figure S7: SEM image of laser etched FTO substrate.

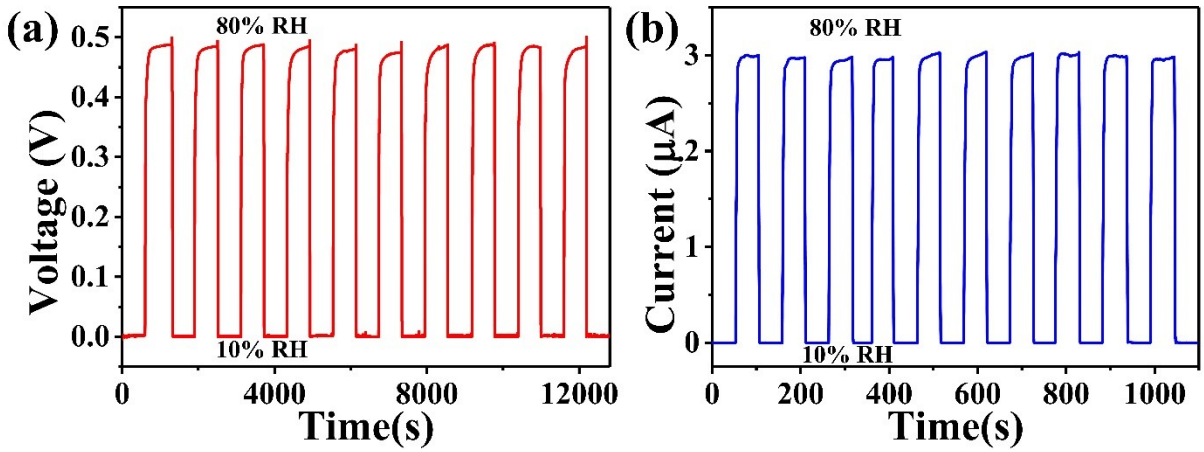

Figure S8: (a) V_{oc} and (b) current dynamic characteristics at 10% RH and 80% RH.

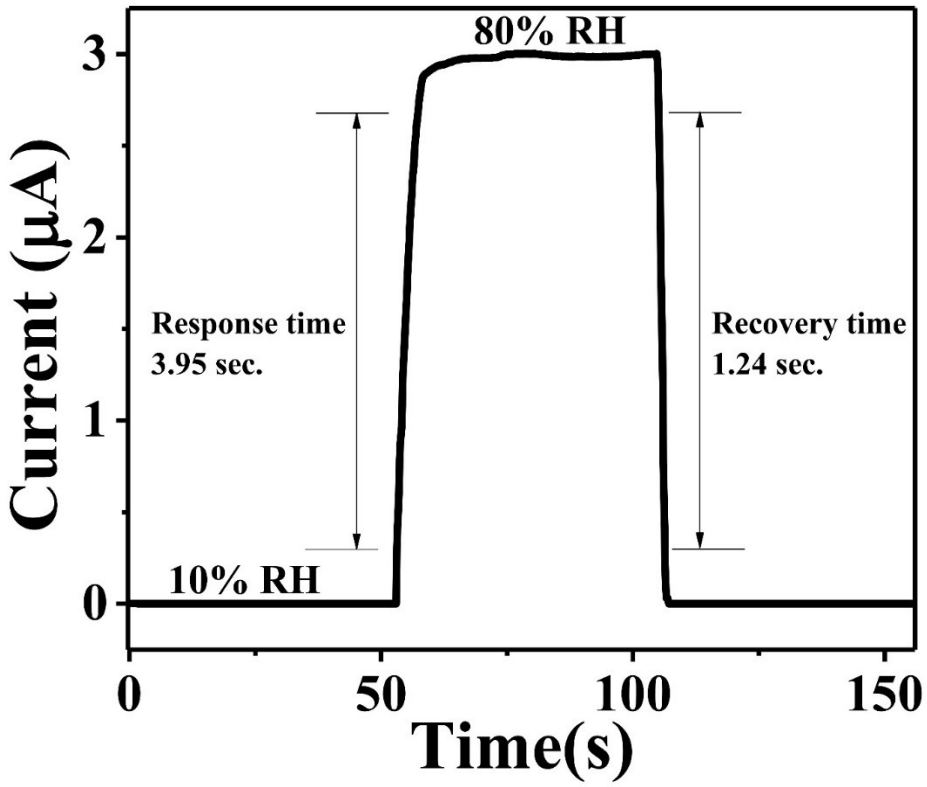

Figure S9: Response time and the recovery time between 10% RH and 80% RH.

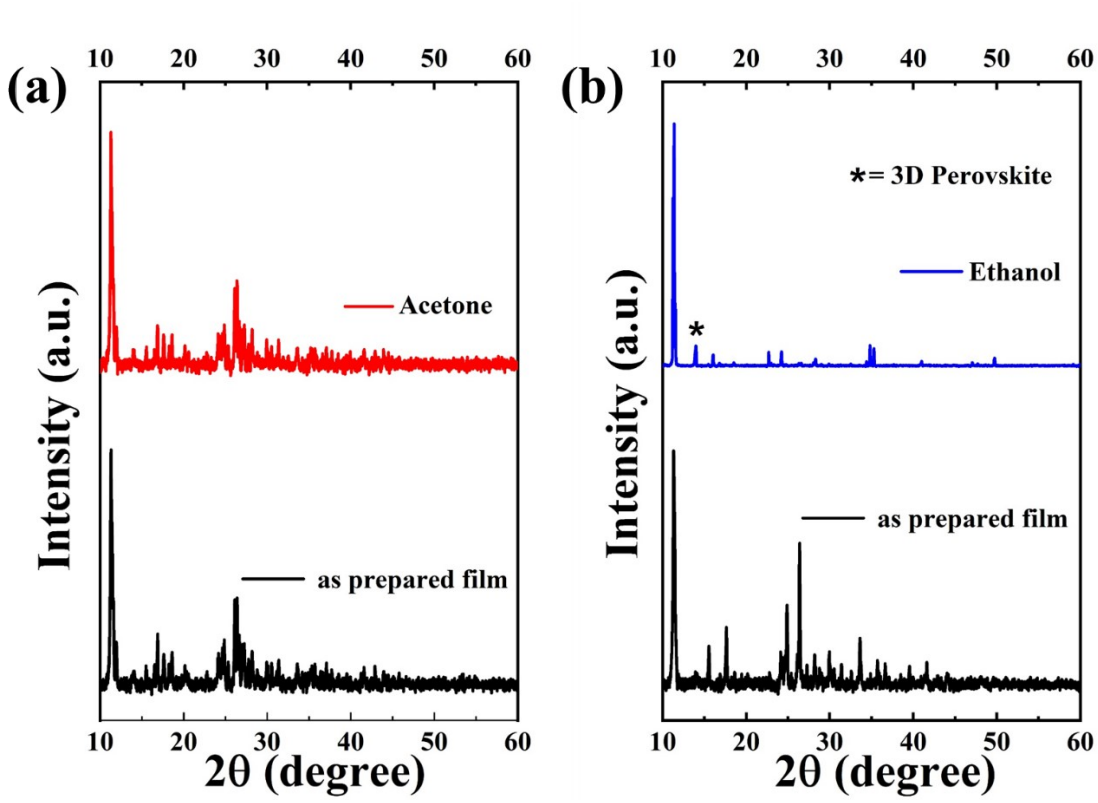

Figure S10. XRD Patterns obtained after exposure to (a) acetone and (b) ethanol vapours for 1 hr.

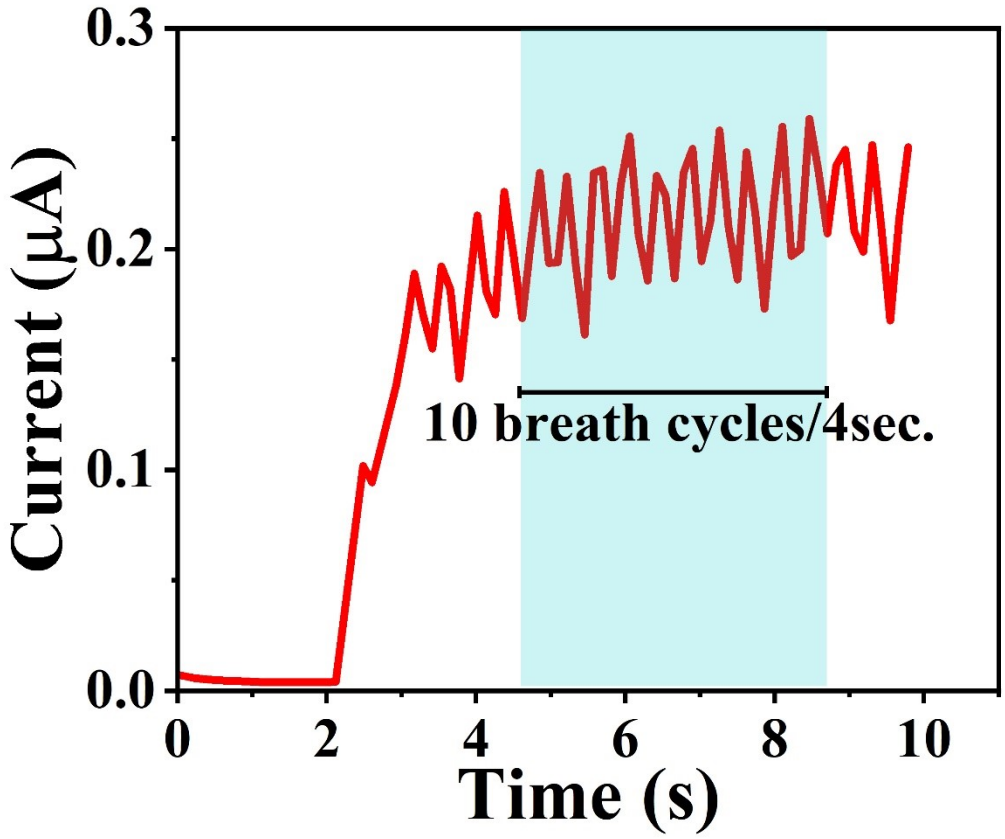

Figure S11: Short circuit current response to fast breathing and the specified time period shows the number of breath cycles per 4 seconds.

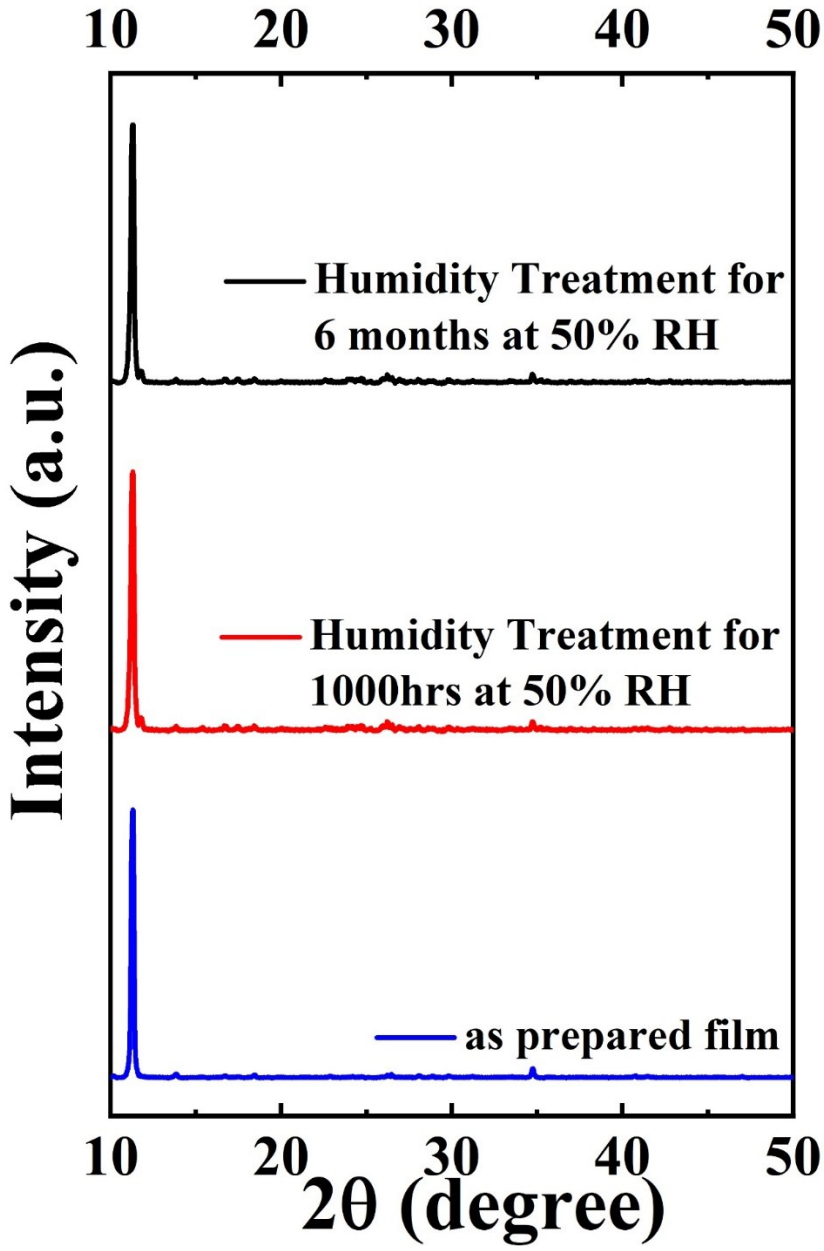

Figure S12. XRD patterns obtained after exposing the sensing material to 1000 hrs and 6 months at an average humidity of ~50% RH